TAILORING POLYPHOSPHAZENES FOR AIRCRAFT FIRE-RESISTANT APPLICATIONS

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ABSTRACT

Phosphazenes, both cyclic and polymeric, have been examined for their application as flame-retardant materials and as flame-retardant additives to organic polymers. A blend of poly[bis(carboxylatophenoxy)phosphazene] with polyurethane precursors resulted in a urethane foam which exhibited increased thermal stability relative to the pure polyurethane. In addition, miscible blends of poly[alkoxyphosphazenes] with organic polymers have been studied. Phosphorylation of a functionalized phosphazene resulted both in a novel elastomer with excellent thermal stability and in a new class of oligomeric flame-retardant additives. Efforts have been made to control the architecture and reactivity, and thus the mixing properties, of phosphazenes using techniques such as the "living" cationic polymerization of phosphoranimines. Block copolymers of phosphazenes and organic polymers are being developed for application as blending agents and flame-retardant materials.

INTRODUCTION

Some of the most effective flame retardants are compounds that contain both phosphorus and nitrogen. Polyphosphazenes are a unique class of polymers with a backbone composed of alternating phosphorus and nitrogen atoms. The versatility of this polymer system is due mainly to the ease of modification of the precursor polymer poly(dichlorophosphazene). The highly reactive P-Cl bonds in this intermediate can be easily replaced by reaction with alcohols, amines, and organometallic reagents as shown in Scheme 1. Appropriate selection of the side groups allows control of the solubility, crystallinity, bioactivity, and surface characteristics. These properties have in turn resulted in a broad range of uses including non-burning fibers or foams and as flame retardants.[1,2] The thermal behavior and decomposition of a variety of polyphosphazenes have been studied in some detail.[3-6] At elevated temperatures, the thermal response depends on the types of side groups present. Polyphosphazenes, especially those that bear aryloxy side groups, possess a high temperature stability as well as excellent flame resistance. In the present work, we describe efforts to increase the flame resistance of polyphosphazenes while developing less expensive, more controlled methods for their synthesis. We have also incorporated phosphazenes into organic polymers in order to impart flame resistance to systems that are normally highly combustible.

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Scheme 1
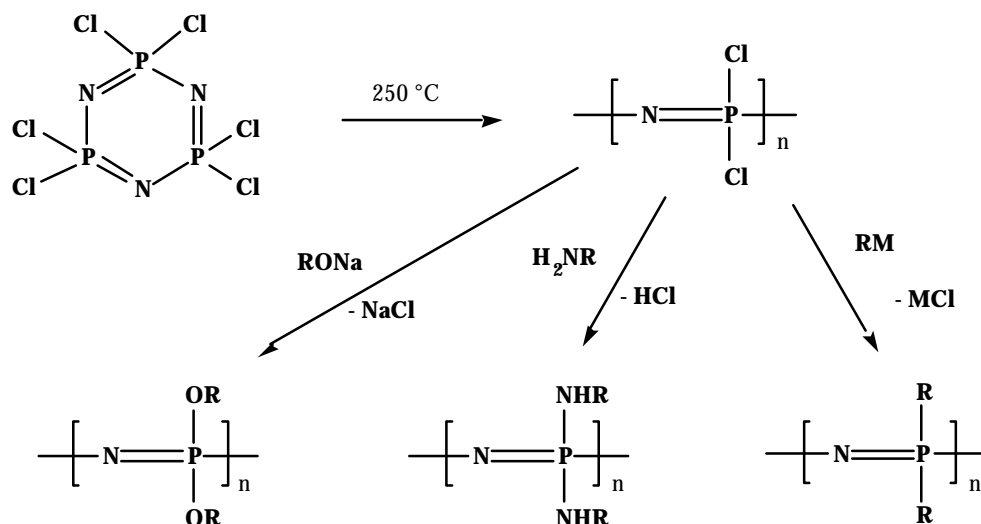
POLYURETHANE / POLYPHOSPHAZENE BLENDS

Polyurethanes are a good example of a traditional organic polymer system that has useful structural and mechanical properties, but is limited by its low thermo-oxidative stability. Although many varieties of this polymer are widely used in aerospace applications and home construction, they are highly combustible.[7] Polyurethanes could be made fire resistant if they were blended with a polymer that would modify the decomposition mechanism of the polyurethane, release noncombustible gases, and/or undergo reactions during heating to create a thermally insulating char to quench further combustion. However, the choice of suitable polymeric flame-retardants is restricted to species that allow retention of the advantageous mechanical properties of the polyurethane. *In situ* chemical reactions between two polymers in a mixture ensures intimate mixing and, given the appropriate chemistry, numerous graft and interpenetrating networks can be designed. We have synthesized composites of a structural polyurethane and poly[*bis*(4-carboxylatophenoxy)phosphazene] (**1**) as illustrated in Scheme 2. The thermal stability and flame resistance of these composites were analyzed.

Preparation and Analysis of Foams

A predetermined quantity of polymer **1**[8] and the hydroxyl terminated prepolymer (Bayer Corp.) were placed in a tared 50 ml polyethylene beaker to achieve a total reactant weight of 8.0 grams. The mixture was hand mixed with a spatula for a period of 5-10 min. The isocyanate terminated prepolymer (Bayer Corp., 8.0 g) was then added to the composition with rapid stirring. As the reaction began to occur, the mixture was extruded between two Teflon coated steel sheets approximately 0.5 cm apart. The resultant foam formed a circular disk which was allowed to cool for 2 h. The foam disk was removed from between the steel plates and was cut into samples with uniform thickness.

Scheme 2

1
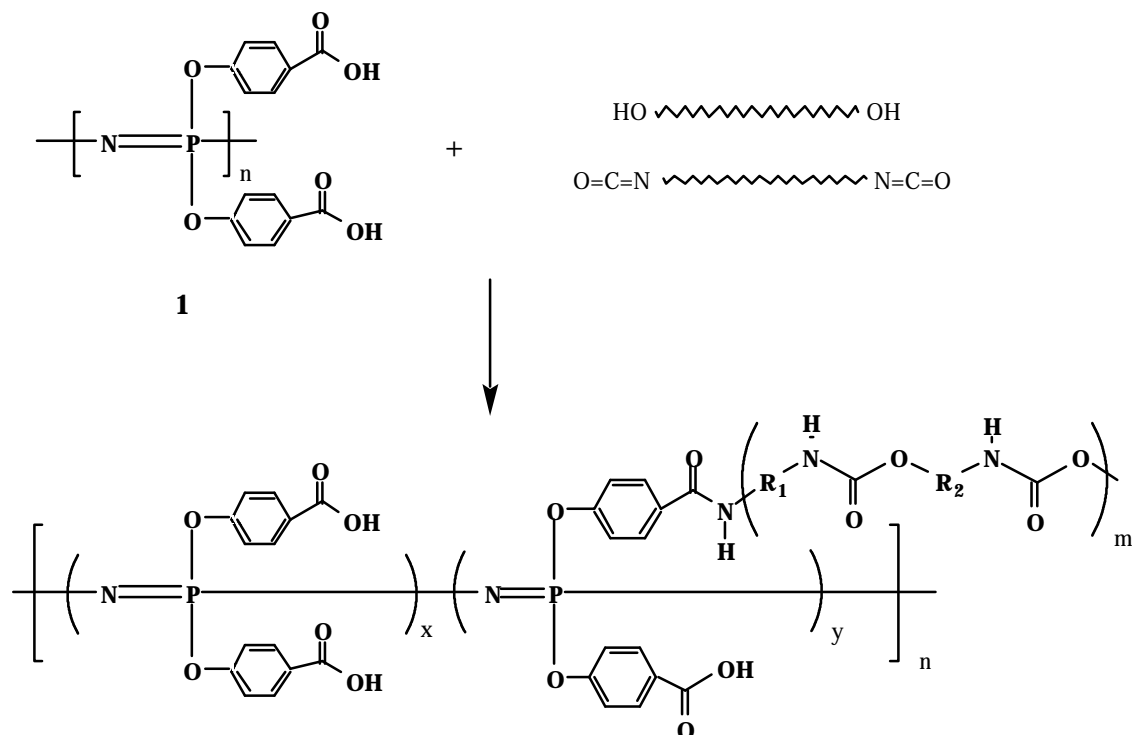
The initial flammability testing of the material was carried out utilizing a horizontal burner test. Bars of dimension 0.5 in. (1.27 cm) x 5.0 in. (12.7 cm) were cut from the foam disk and marked at 0.75 in. (1.91 cm) from each end. A Bunsen burner was ignited away from the sample and adjusted so that the flame was 0.75 in. (1.91 cm) long with the tip of the flame being slightly yellow. The burner was then moved into position directly below the sample and allowed to remain at the site until the sample burned to the first line on the sample or 30 sec, whichever occurred first. Once the burn front reached the first line, the time of burning between the first and last mark was measured. The average burning time and extent of burning were then determined. Oxygen index (OI) measurements were obtained on an instrument constructed according to ASTM-D-2863-91 using Type C specimens. The OI of a material is a measure of the minimum concentration of oxygen (in a controlled atmosphere of nitrogen and oxygen) necessary to sustain combustion of the material when ignited.

Flammability Tests

Polyurethanes, in the absence of flame retardants, are extremely combustible. In these tests, the pure polyurethane sample burned rapidly after exposure to the flame and was totally consumed within 40 sec, to leave a black char. A 5-15 wt% loading of **1** had little effect on the overall combustibility of the samples. However, at a 20 wt% loading of **1**, the samples self-extinguished. After the full 30 sec limit had elapsed and the flame was removed, the sample slowly extinguished and was completely self-extinguished after a total of 55 sec. The internal two-thirds of the charred region remained unchanged with no evidence of combustion. The outer

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one-third formed a black glassy char which had apparently provided a protective coating over the bulk of the sample. Polymer **1** is a high char yielding material,[6] and this char can coat the more combustible components and prevent further combustion. Also, previous work indicated that polymer **1** releases a large amount of carbon dioxide during pyrolysis, thus increasing the percentage of noncombustible gases present.[6]

Although the above results are qualitatively encouraging, it must be emphasized that horizontal burn tests can produce misleading (usually over-optimistic) results. Oxygen index (OI) measurements were subsequently performed on blends containing 0, 5, 10, and 20 wt% polyphosphazene **1** (Table 1). The results obtained on the foams containing 5 and 10 wt% polyphosphazene (0.5 and 1.0% P) were identical, within error, to that measured for the pure polyurethane foam (OI = 20.0 ± 0.02). This is consistent with the results obtained from the qualitative horizontal burn test which indicated that at loadings of less than 20 wt% polyphosphazene, there was minimal effect on flammability. However, the foam containing 20% phosphazene (~ 2 wt% P) showed an increased OI of 21.5 ± 0.2. Although this is not a striking increase, and does not match the dramatic visual horizontal burn test observation, the trend is correct. We believe that the ~ 2 wt% total phosphorus in this polyurethane/polyphosphazene mixture represents the lower limit required to impart meaningful flame resistance.
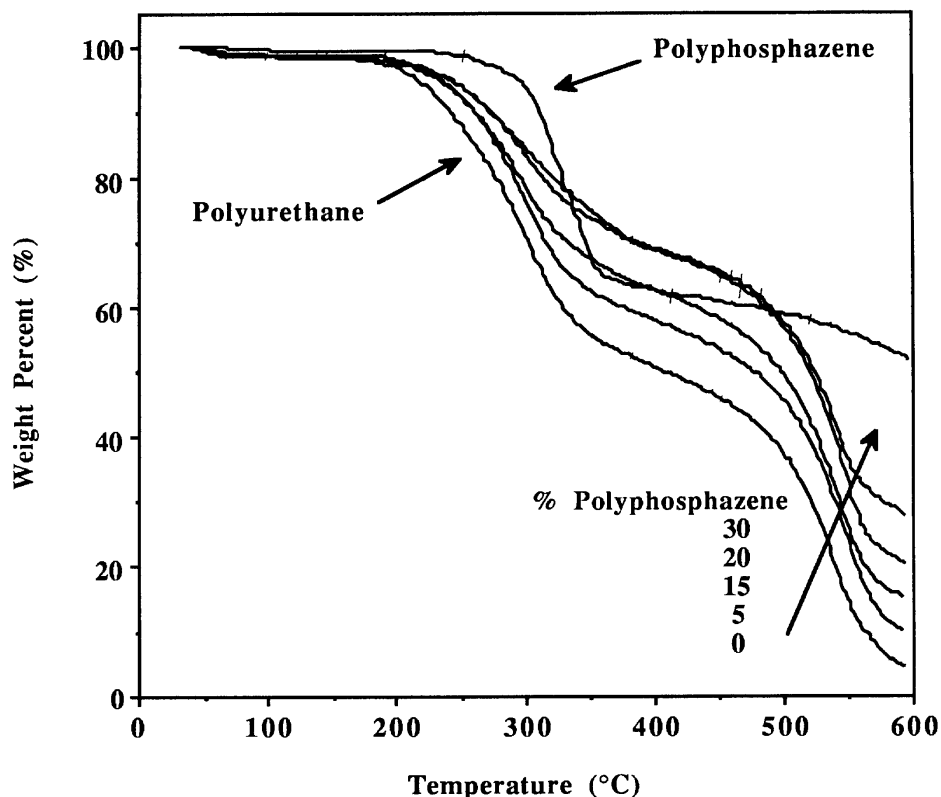
Table 1. Polyurethane/polyphosphazene foams

Wt % Phosphazene	Wt % Phosphorus	OI	Char at 600 °C (%)
0	0	20.0	5
5	0.5	20.0	10
10	1.0	20.0	12
20	1.9	21.5	20

Thermal Analysis

In general, poly[*bis*(*p*-R-phenoxy)phosphazenes], where R is a polar substituent, give high char yields of 50% or more at temperatures at or above 700°C and also undergo a high degree of cross-linking to form a dense ultrastructure.[3, 4] Polymer **1** undergoes skeletal cleavage and cross-linking reactions when heated.[6] The onset of cross-linking occurs at 200°C, resulting in the small weight loss detected by TGA (Figure 1). Continued pyrolysis results in a further 35% weight loss at 320°C, associated primarily with the loss of carbon dioxide. This is followed by the slow continuous weight loss of benzoic acid and a 55% char yield at 600°C.

The thermal weight loss (TGA) curve for the pure polyurethane in air is also shown in Figure 1. The onset of thermal degradation occurs at ~ 200°C, and the maximum rate of degradation for the two main decomposition steps occurs at ~ 300°C and 540°C. Because the foamed blends contain relatively small amounts of polymer **1**, the TGA curves (Figure 1) have the same general shape as that of the pure polyurethane. However, as the concentration of the polyphosphazene in the mixture is increased from 5 to 20 wt%, the TGA curves appear to be displaced along the temperature axis towards higher temperatures. Significantly, above a 20 wt% loading of polymer **1** (where enhanced flame resistance in the horizontal burn test and OI measurements

was detected) the TGA curves are essentially identical, except in the region between 550 - 600°C. Here the amount of char approximately parallels the amount of **1** initially present in the mixture. The overall char yield at 600°C is actually higher than expected based on the original composition of the samples. For example, the sample with 30 wt% **1** has a char yield of ~ 30% at 600°C. Based on the data obtained for the individual components, only ~ 20% char yield is expected. An explanation for this is that the high char of polymer **1** either entraps volatile molecules or limits the thermo-oxidative degradation of the polyurethane.

Figure 1. TGA curves for the polyurethane, polyphosphazene, and polyurethane / poly(organophosphazene) foams containing 5, 15, 20, and 30 wt% of polymer **1**.

PHOSPHORYLATION OF PHOSPHAZENES

One of the reasons that phosphazenes have excellent flame retardant properties is the presence of both phosphorus and nitrogen in the backbone. In organic polymer systems, the addition of small-molecule phosphorus compounds (particularly phosphorus esters) is one of the most effective ways to decrease the flammability of the system.[9] Extensive work has been carried out on the incorporation of phosphorus into organic polymers by way of small molecule or polymeric additives, copolymerizations, and chemical modification.[10, 11] The effect on combustion of the polymer depends on the chemical structure of the macromolecule, and is commonly attributed either to the generation of polyphosphoric acid and subsequent char

formation, or to a modification of the decomposition mechanism of the polymer.[9, 12, 13] Although polyphosphazenes already have a significant phosphorus content, improved fire resistance could result from the introduction of phosphate or phosphonate species into the side groups.

We have synthesized novel aryloxyphosphazenes, both cyclic and polymeric, that bear pendent phosphate groups. These groups were chosen to be analogues of commonly used flame retardant additives such as triethyl phosphate and triphenyl phosphate.[9] Immobilization of the phosphate units on the phosphazene was expected to increase the thermal stability and flame resistance of the polymers without impairing the mechanical properties by plasticization. Phosphorylated cyclic trimers were synthesized as model compounds for the high polymers and as possible small-molecule additives. These trimers were blended with polystyrene and evaluated for their performance as oligomeric flame retardant additives. The thermal stability of the phosphorylated polymers has been studied and compared to those of non-phosphorylated phosphazenes.

<u>Synthesis of Phosphorylated Phosphazenes</u>

Phosphazenes bearing phenolic functionalities[14] were induced to react with halogenated phosphate esters as shown in Scheme 3. The reactions involving diethyl chlorophosphate required longer reaction times than did the reactions with diphenyl chlorophosphate. At the high polymer level, full conversion of the hydroxyl groups to diethyl phenylphosphate species did not occur, and the resulting product was slightly crosslinked. Phosphorylation of **3** with diphenyl chlorophosphate was much easier, with full conversion obtained at room temperature. This polymer dissolved and precipitated very well, giving a light brown, fibrous material.

Scheme 3

2 : n = 3
3 : n = 40

4 : n = 3, R = Et
5 : n = 3, R = Ph
6 : n = 40, R = Et
7 : n = 40, R = Ph
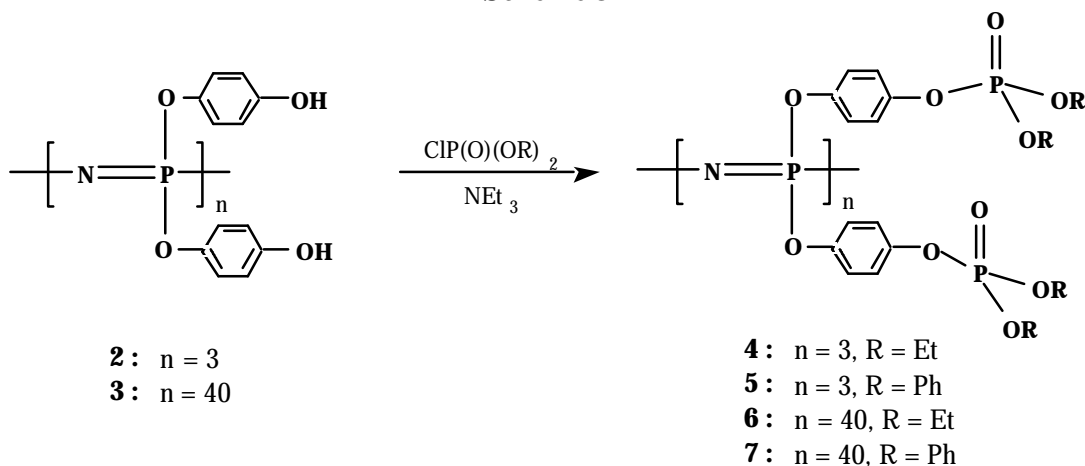
<u>Thermal Analysis</u>

The TGA curves for the products of the phosphorylation of **3** are shown in Figure 2, together with the curve of polymer **3** for comparison. Polymer **6**, which contained residual aromatic hydroxyl groups, showed an intial decomposition similar to that found for **3**. This decrease in initial thermal stability is typical of polymers with phosphate additives and is due to

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volatilization of the phosphorus ligands during polyphosphoric acid formation.[10, 13] Polymer **7** showed significant improvement in its initial weight loss temperature, with no signs of the initial decomposition characteristic of **3**. Both phosphorylated polymers showed a decrease in final char yield, and this was probably due to the loss of the phosphate ligands during the decomposition. Polymer **7** had more phosphate present and less initial crosslinking than did polymer **6**, which may explain the difference in relative char yields.
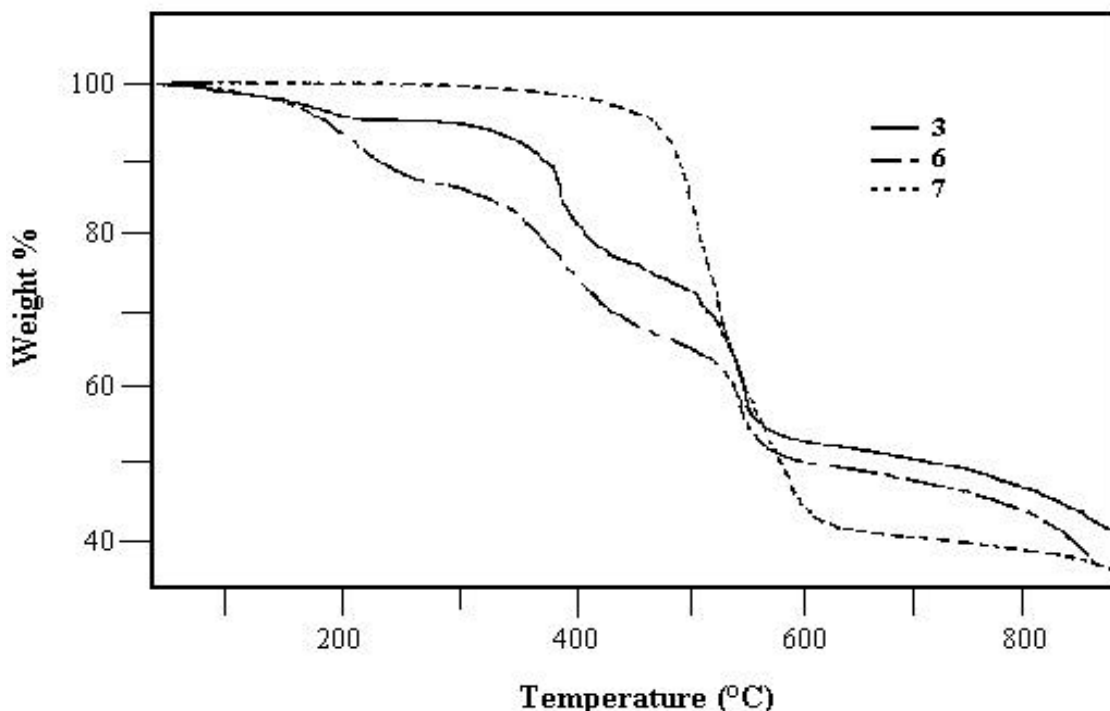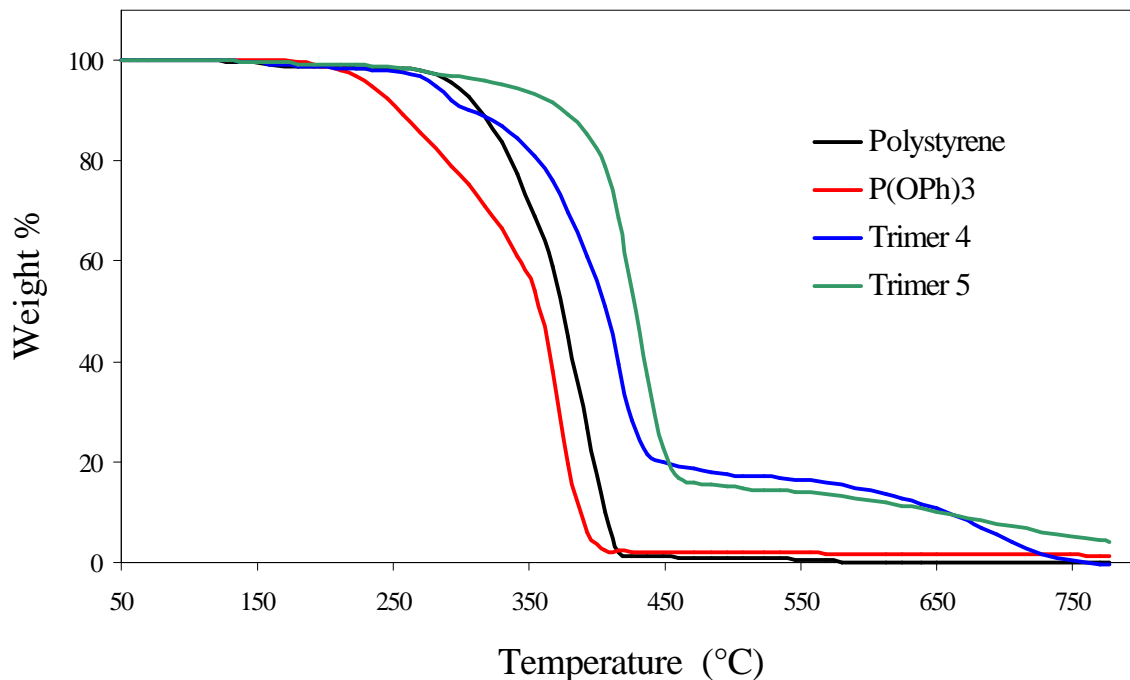

Figure 2. Loss in weight with temperature of polymers **3**, **6**, **7**.

Flame Retardance of Polystyrene

Triphenyl phosphate and cyclic trimers **4** and **5** were mixed with polystyrene at 0, 10, 20, and 30 wt% to give total solids of 5g. These mixtures were dissolved in 50 mL methyl ethyl ketone (MEK) and cast into molds measuring 22.5 cm x 17.5 cm. Slow evaporation of the solvent was ensured by covering both the mold and a reservoir of pure MEK with a loose covering of foil. After 5 hours, the samples were dried in a vacuum oven at 40 °C for 72 hours to produce films of thickness 0.15 mm. The films containing triphenyl phosphate or **5** were transparent, while the films containing **4** were opaque.

Because low molecular weight phosphorus compounds tend to volatilize under normal processing conditions, oligomeric phosphate derivatives are often used to enhance the thermal stability and flame resistance of polystyrene.[15] The relatively high molecular weights of the cyclic trimers reported here make them excellent candidates for flame retardant additives. Figure 3 shows the TGA curves in air for polystyrene mixed with triphenyl phosphate and trimers **4** and **5** at 30 wt% loadings as well as for the pure polymer. Unmodified polystyrene begins to

decompose at 290°C and loses weight rapidly until 425°C. The addition of triphenyl phosphate lowered the initial decomposition temperature to 200°C, due to the volatilization of the phenyl ligands, and left minimal char yield at 750°C. The initial decomposition temperature of polystyrene was also lowered by the addition of trimer **4**, but a substantial char yield is formed between 450°C and 650°C. Excellent thermal stability was observed for the polystyrene that contained trimer **5**. Drastic weight loss did not occur until 380°C and ended at 460 °C with 16% residual weight.

Figure 3. Loss in weight with temperature of polystyrene containing 30 wt % triphenyl phosphate, trimer **4**, and trimer **5**.

Triphenyl phosphate gives a good flame retardant behavior as shown in Table 2 by the increase in oxygen index (OI) with increasing weight percent additive. However, this improvement in flame resistance comes with a deterioration in mechanical properties. The polymer containing 30 wt% triphenyl phosphate had a glass transition at room temperature, and gave a film that was very pliable. Despite having the highest phosphorus content of the three additives, phosphazene **4** did not dramatically enhance the flame resistance of polystyrene. This was probably due to phase separation between the polymer and the trimer even at low loadings, which minimized the interaction between the polymer and the additive. Phosphazene trimer **5** demonstrated the best overall flame retardant behavior. Both the 10 and 20 wt% loadings resulted in an increase in the OI relative to the same loadings of triphenyl phosphate. Polystyrene containing 30 wt% additive showed a slight decrease in the OI relative to films containing 30 wt% triphenyl phosphate, but films with this loading tended to flow more during combustion than did the films with lower loadings, and this resulted in easier flame spreading.

This trimer had only a slight plasticizing effect on the polymer compared to triphenyl phosphate. Even at 30 wt% additive, the glass transition was well above room temperature.
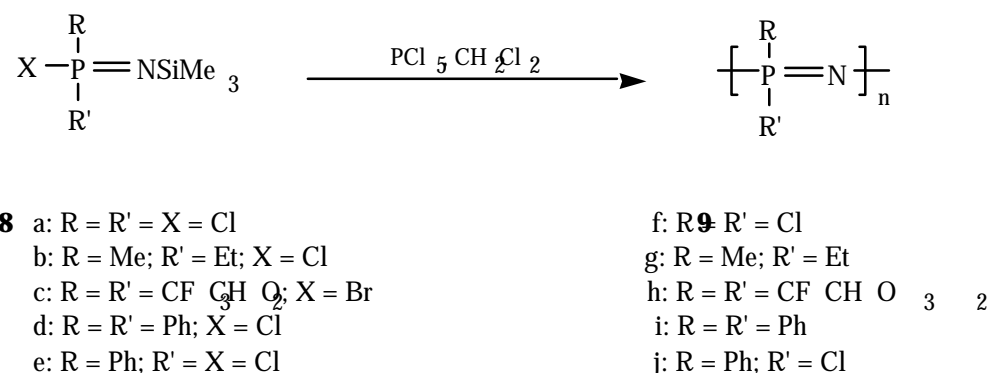
Table 2. Polystyrene containing flame retardant additives

Additive	wt%	P wt%	T_g (°C)	OI
	0	0	100.6	18
Triphenyl phosphate	10	0.95	68.3	22
	20	1.90	48.9	24
	30	2.85	25.3	27
Cyclic trimer **4**	10	1.74	86.5	19
	20	3.47	85.3	20
	30	5.21	84.5	22
Cyclic trimer **5**	10	1.28	90.8	24
	20	2.55	84.8	26
	30	3.83	77.5	25

POLYPHOSPHAZENES WITH CONTROLLED ARCHITECTURES

The synthesis of poly(dichlorophosphazene) has traditionally been carried out by a thermal ring-opening polymerization of hexachlorocyclotriphosphazene as shown in Scheme 1. This high temperature synthesis offers no control over chain length, molecular weight distribution, or polymer architecture.[16] An improved synthesis of polyphosphazenes involves the "living" cationic polymerization of phosphoranimines as shown in Scheme 4. This polymerization proceeds under mild conditions and produces poly(dichlorophosphazene) (**9**f) with living ends that can initiate further polymerization. Molecular weights are controlled by changing the monomer-to-initiator ratio, and polydispersities are typically less than 1.3 for degrees of polymerization up to 150.[17] This synthesis has also been extended to the polymerization of organo-substituted phosphoranimines (**8**b-e) to produce

Scheme 4

$$X \!-\! \underset{R'}{\overset{R}{\underset{|}{\overset{|}{P}}}} \!=\! NSiMe_3 \quad \xrightarrow{\text{PCl}_5\ \text{CH}_2\text{Cl}_2} \quad \left[\underset{R'}{\overset{R}{\underset{|}{\overset{|}{P}}}} \!=\! N \right]_n$$

8 a: R = R' = X = Cl
   b: R = Me; R' = Et; X = Cl
   c: R = R' = CF$_3$CH$_2$O; X = Br
   d: R = R' = Ph; X = Cl
   e: R = Ph; R' = X = Cl

9 f: R = R' = Cl
   g: R = Me; R' = Et
   h: R = R' = CF$_3$CH$_2$O
   i: R = R' = Ph
   j: R = Ph; R' = Cl

poly(organophosphazenes) (**9**g-j).[18] Because molecular weight, polydispersity, and macromolecular architecture all affect polymer properties, the versatility of polyphosphazenes can be greatly expanded by designing both chain architecture, side groups, and functional end groups.

Architectural control of phosphazenes via this new route has been obtained through the use of fully substituted phosphoranimines (**10**) as illustrated in Scheme 5.[17] If R' bears multiple amine functionalities, **10** can act as a multifunctional initiator, and star-branched polymers can be formed.[19] If R' contains a functional group that has been protected or that is unaffected by the polymer synthesis, then **10** can be converted into an initiator (**11**), giving a mono-telechelic polymer, or can be used as an end-capping agent for mono- and di-telechelic polymers. Conversion of these end groups to reactive functionalities opens up the possibility of formation of multi-block copolymers with condensation-type organic polymers. This concept has also been appled to the synthesis of di- and tri-block copolymers of phosphazenes with organic polymers. As shown in Scheme 6, amine-terminated poly(ethylene oxide) reacts with a phosphoranimine, which is then converted into an initiator for polymerization of the phosphazene monomer.[20] This process allows a combination of phosphazenes and organic polymers in ways that have been inaccessible up to this time. This access to phosphazene-organic linear block copolymers and star structures is expected to be used to make polyphosphazenes that are compatible with combustible organic polymers or which concentrate in the surface regions of a polymer to maximize the fire resistance properties.

Scheme 5
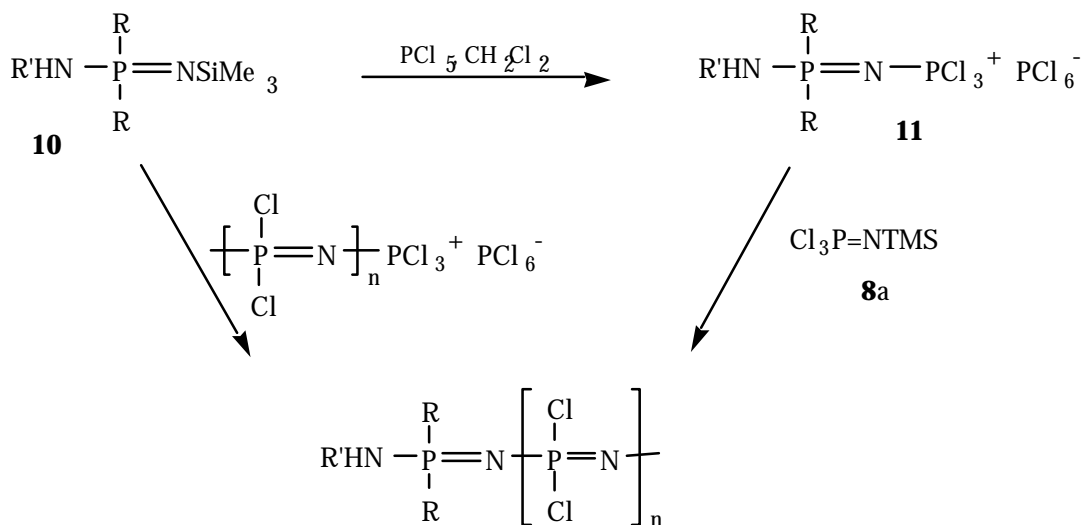
An important feature of this "living" cationic polymerization is that the reaction occurs at ambient temperature and pressure. Most phosphazene polymerizations require high temperatures, and some can eliminate corrosive byproducts. Also, a new synthetic route has been developed that yields either hexachlorocyclotriphosphazene and trichlorophosphoranimine (**8**a).[21] This reaction requires less extreme temperatures than are normally required to make either the trimer or the monomer. The product distribution can be tailored by modification of the reaction conditions, and overall yields are much higher than from previous synthetic routes.

Scheme 6
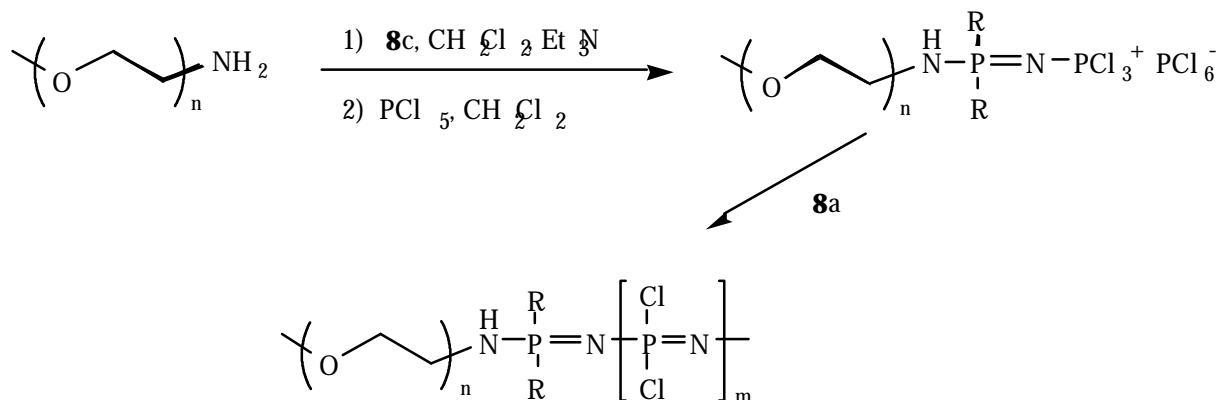
HEAT RELEASE DATA

      Pyrolysis-combustion flow calorimetry (PCFC) has been performed on selected polyphosphazenes by Richard Lyon and co-workers. These data are summarized in Table 3. The heat release capacities (η_c) of **A** and **I** are within the range of 30-50 J/g-K found for high performance thermosets and thermoplastics (PEEK, phenolic resins). All of the polymers except the alkoxyphosphazenes have η_c's lower than commodity plastics (PET, nylon; 250-350 J/g-K) and polyolefins (500-600 J/g-K). Typically, fluoroalkoxy derivatives **F** and **G** show negligible

Table 3. PCFC Data for [-NP(OR)(OR')-]$_n$*

		R, R' (Ø = aromatic)	η_c (J/g-K)	Q_c (kJ/g)	μ (%)
Aromatic	**A**	-Ø-OH (**3**)	48	12.2	49
	B	-Ø-CH$_2$CH$_3$; -Ø	64	9.1	48
	C	-Ø-OCH$_2$Ø	74	17.5	51
	D	-Ø-OCH$_3$	90	15.3	49
	E	-Ø	210	21.8	26
Halogenated	**F**	-CH$_2$(CF$_2$)$_3$CF$_2$H ; -CH$_2$CF$_3$	67	7.6	2
	G	-CH$_2$CF$_3$	110	7.7	1
	H	-Ø-Br	153	10.4	24
Phosphorylated	**I**	-Ø-P(O)(OCH$_2$CH$_3$)$_2$ (**6**)	48	11.6	55
	J	-Ø-P(O)(OØ)$_2$ (**7**)	120	17.5	36
Alkoxide	**K**	-CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$	255	22.9	12
	L	-CH$_2$CH$_2$CH$_2$CH$_3$	463	27.0	23

    *Data provided by Dr. Richard E. Lyon (FAA)

char at 700°C in an oxygen-free atmosphere (μ); however, both have good flame resistance as predicted by their low η_c's. The trend in η_c for **A** and **C-E** are consistent with previous findings that thermal stability can be correlated with the reactivity of substitutents in the *para-* position and thus with the ability of the polymer to crosslink before depolymerization occurs. This concept can also be applied to polymers **I** and **J**. Polymer **B** is especially interesting since there is no high temperature reactivity difference between it and polymer **E**, yet the flame resistance is dramatically increased. The char of **B** is also higher than that of both **E** and poly[*bis*(4-ethylphenoxy)phosphazene]. It is possible that morphology plays a role in this behavior since **B** is amorphous, whereas the corresponding homopolymers are crystalline.

FUTURE WORK

We are currently investigating the synthesis of poly(norbornene) bearing phosphazene cyclic trimers as side groups.[22] Possible improvements in the solvent resistance and mechanical properties of this class of rubber are being studied, and preliminary results indicate that these polymers show an increased thermal stability relative to unmodified poly(norbornene). Phosphazene / organic polymer block copolymers are being developed to modify both the thermal and the mechanical properties of organic polymers. Improvements in the syntheses of polyphosphazenes and their precursors is also continuing. Finally, questions regarding the effects of polymer morphology and side group reactivity on the flame resistance of polyphosphazenes still need to be answered in order to design the best possible flame retardant materials.

ACKNOWLEDGEMENTS

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